

ASSESSMENT OF SOME ANALYTICAL PROCEDURES FOR THE EXAMINATION OF THE ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL PROCESS

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Owing to the sophisticated character of modern biological wastewater treatment systems, the diagnosis of the mechanisms and interactions involved has become extremely difficult. Further difficulties in their scientific clarification can be generated by some of the analytical procedures used. The primary objective of the study reported on in this paper was to demonstrate that under certain conditions, e.g. during Enhanced Biological Phosphorus Removal, the commonly recommended analytical methods fail to produce reliable results. This holds primary for the examination of COD, assessment of Ca and Mg concentration variability, or procedures of collection and preparation of samples, where the results obtained may differ considerably, depending on the method used. These differences lead to incorrect assessments of, and conclusions on, efficiency, stoichiometry and kinetics of the EBPR process and thus blur the precision of assessing how different parameters affect the process.

Keywords: Wastewater treatment, phosphorus removal, analytical procedures, calcium, magnesium, chemical oxygen demand

1. INTRODUCTION

Owing to the strict demands made on the quality of the wastewaters discharged into the environment, wastewater treatment plants have developed in most instances into complex, multiphase systems allowing the co-removal of organic carbon, together with nitrogen and phosphorus compounds. This integrated C, N and P removal is possible only under conditions favouring the occurrence of such biochemical processes as: organic carbon compounds oxidation, ammonification, nitrification, denitrification and Enhanced Biological Phosphorus Removal (EBPR). In practice, such conditions are achieved by operations supporting privileged growth of microorganisms responsible for these processes. These favorable conditions depend on diverse environmental factors (supply of energy

substrates, amount of dissolved oxygen, redox potential, temperature, etc.) or on the control of the process parameters (hydraulic retention time (HRT), solids retention time (SRT), etc.). There are also some other factors supporting the occurrence of the said biochemical processes in individual wastewater treatment systems, e.g. the type or volume of the reactors used, the sequence of particular stages in the treatment train, the application of wastewater and/or sludge recirculation, and the modes by which they are recirculated.

Owing to the sophisticated character of contemporary biological wastewater treatment technologies, which involve:

- simultaneous occurrence of different biochemical operations,
- a diversity of microorganisms in the activated sludge population,
- different physical and chemical environments,
- the effect of technological parameters,

a detailed diagnosis and clarification of the mechanisms governing individual biochemical operations, as well as the determination of relevant interactions, have become extremely difficult.

This problem seems to be best exemplified by the EBPR process. In spite of its widespread use in full-scale wastewater treatment plants in the past decade, the EBPR process itself is still far from being well recognized and understood. This is why those systems suffer from periodical failure, which creates operational problems. A review of investigations into the parameters that influence the performance and efficiency of the EBPR process reported in specialized literature has shown a considerable diversity of results and conclusions (Mulkerrins et al., 2004). It should be emphasized that this diversity often concerns the key issues dealt with when assessing the EBPR mechanisms, e.g. the role of organic compounds supply, the competition of Phosphate Accumulating Organisms (PAO) with Glycogen Accumulating Organisms (GAO), the unfavorable influence of nitrites and nitrates or the contribution of metal cations to the phosphorus removal mechanisms. This caused that the main EBPR metabolic models developed so far, e.g. by Comeau-Wentzel, Mino or Smolders, (described in detail by Comeau et al., 1986; Grady et al., 1999; Łomotowski et al., 1999; Mino et al., 1998; Smolders et al., 1995), seem to be inadequate for universal assessment of the various factors that influence the EBPR mechanisms and efficiency.

The problems encountered in the scientific identification of the mechanisms governing the EBPR may result not only from the complex character of the biochemical processes occurring in anaerobic-anoxic-aerobic wastewater treatment systems. From the author's previous experience gained during his experimental research into the influence of chloride and sulphate ions on the EBPR process (Zdybek, 2004) it follows that the analytical method used could have also significantly influenced the observed wastewater treatment mecha-

nisms. The same experimental research has revealed that the use of different measurement procedures, especially those for the examination of COD, calcium and magnesium concentrations, may be responsible for the great diversity of results. The procedures made use of for sample collection and preparation can also considerably affect the quality of the results. Thus, when use is made of different analytical procedures, this will influence the assessment of efficiency, stoichiometry and kinetics. And this may also blur the precision of assessing how different parameters affect the course of biochemical processes.

It seemed worthy to present problems that arise from the application of various analytical procedures for the determinations of COD, Ca and Mg concentrations, as well as for the collection and preparation of samples. The interpretation of the mechanisms governing the EBPR process on the basis of the results obtained in this way differs significantly from one analytical method to another.

The suggestions made in this paper as to how to eliminate or at least minimize the adverse influence of the analytical procedures on the assessment of the EBPR may be useful especially for further investigators of the process.

2. MATERIALS AND METHODS

The research on the EBPR process was carried out in a laboratory-scale sequencing batch reactor system. Synthetic wastewater was treated continuously in a 6.0 h cycle consisting of: short filling, 2.5 h anaerobic phase, 2.5 h aerobic phase and 0.75 h sedimentation phase followed by a short stoppage period in order to discharge the treated wastewater. Excess sludge was removed at the end of each aerobic phase. There was no pH adjustment in the reactors. The experimental conditions allowed a full inhibition of the nitrification process. More detailed information on the experimental conditions can be found elsewhere (Zdybek, 2004; 2005).

3. ASSESSMENT OF ANALYTICAL PROCEDURES

3.1. Collection and preparation of samples

Generally, the procedures used for sample collection and preparation are the key factors responsible for the accuracy and interpretation of the results obtained. Optimally, these procedures should eliminate the potential of probe contamination. Thus, sampling should be carried out as soon as possible, without any drastic change in the environment of the probe (e.g. in the pH, dissolved gases concentration, especially in oxygen and carbon dioxide, etc.). Otherwise, a number of undesirable phenomena (precipitation, dissolution, volatilization or satura-

tion) may occur as a result of chemical and/or biochemical processes, thus influencing – quantitatively and qualitatively – the interpretation of the results obtained.

Such problems were faced in the course of our research, where the results of analyses of suspended solids (in activated sludge) and dissolved substances (in wastewater) raised doubts. Initially, sludge was separated from the wastewater by filtration through filter paper according to relevant Polish standards: PN-72/C-04559, PN-78/C-04541 or PN-EN 872/2000. During filtration, the pH decreased and conductivity increased. There were also differences in phosphate concentration between filtered and centrifuged samples, which influenced the assessment of phosphorus removal efficiency and the kinetics of anaerobic release and aerobic uptake in the course of the wastewater treatment process.

Closer analysis showed that the remarkable quantitative transformations of suspended compounds into dissolved ones, and vice versa, in the samples could be due to the use of distilled water for filter paper flushing. The relatively low pH of distilled water induced the dissolution of calcium, magnesium and phosphate complexes. The variability of their concentrations in the solid and liquid phase was confirmed. Once the procedure of filter paper flushing with distilled water was abandoned, the differences in P, Ca and Mg concentrations between filtered and centrifuged samples became far less distinct, and so did the differences in the pH and conductivity values measured before and after the filtration procedure. Nevertheless, such transformations were still observed during kinetic analysis. It was found that the dissolution or precipitation of calcium and magnesium phosphate complexes could have been induced by pH variations due to the change in dissolved oxygen and/or carbon dioxide concentrations if the filtration procedure had to be extended. For example, oxygen diffusion to the wastewater sample withdrawn from the reactor in the anaerobic phase could have initiated an aerobic metabolism of the PAOs and made them take up phosphates. It may also be the changes in carbon dioxide concentration due to diffusion or stripping that have influenced the pH of the sample, thus accounting for the dissolution or precipitation of phosphate calcium and magnesium complexes according to the mechanisms described in Section 3.3.

These observations, as well as the identification of the analytical problems mentioned, made it possible to work out such methods of sample collection and preparation that would eliminate the undesirable mechanisms influencing the accuracy of analytical methods. Thus, in order to avoid changes in the physical and chemical conditions during collection of the sample it is necessary to minimize such operations that cause its aeration, e.g. mixing, pouring out of one vessel to another and shaking. In the procedure of sample preparation for analysis time seems to be a key factor. Thus, for the sake of accuracy, centrifugation is much better than filtration through the filter paper. If centrifugation is

unfeasible, for example because of the large volume of the probe, the negative effect of filtration time can be minimized by two-step filtration (via high speed filter paper followed by low speed filter paper), which shortens the time of contact between the main part of suspended solids and the solution. While using any of the filtration methods, it is essential to "lose" the initial volume of the sample. When investigating the EBPR process, the flushing of sludge, even with the smallest amount of distilled water, seems to be unacceptable.

Not complying with these recommendations can, in the author's opinion, lead to significant discrepancies, especially when assessing, in quantitative terms, the variability in phosphate, calcium, magnesium, suspended solids and dissolved substance concentrations during the EBPR process.

3.2. COD examination procedure

Chemical Oxygen Demand (COD) is one of the most commonly used parameters for the assessment of the efficiency and kinetics of organic matter removal when analyzing both full-scale and laboratory-scale wastewater treatment systems. The widespread use of the COD assay is mainly due to its simplicity and repeatability. The COD examination procedure is much less time-consuming than, for example, the procedure of Biological Oxygen Demand (BOD) examination and, in contrast to the Total Organic Carbon (TOC) examination procedure, does not need specialized equipment. COD also plays an important role in the research on the EBPR process, where the supply of organic substrates is an essential factor favourizing privileged growth of PAOs. Thus, when analyzing in detail the mechanisms of the EBPR process, it is necessary to examine and compare at the same time the efficiency and/or the kinetics of organic compounds removal and phosphorus concentration changes. In that particular case, the use of the COD assay is undeniably the fastest, the easiest and the cheapest approach, which additionally produces some useful conclusions. For example, according to a literature review of different EBPR systems (Mulkerrins et al., 2004), the proportion of COD to total phosphorus (COD/P) of 40:1 is considered to be favourable for the proper performance of the EBPR. Nowadays, this ratio is practically being used in the design of the EBPR process, in the operation of the EBPR systems, and in the analysis of EBPR performance.

The efficiency of the EBPR process is determined not only by the quantity but also by the quality of the available organic substrates. As shown by many investigators (Abu-Ghararah et al., 1991; Carucci et al., 1997; Randall et al., 1997; Tasli et al., 1997), the presence of acetate is the factor that affects the mechanisms of phosphate removal. For that reason, in many laboratory studies of the EBPR process a definite amount of acetate is often added to the wastewater composition. A similar approach has been attempted in real wastewater tre-

atment plants by introducing, for example, raw wastewater or primary sludge digestion (Malej, 2001).

The presence of large amounts of acetate in the wastewater can raise some analytical problems during COD examination. In the absence of an Ag_2SO_4 catalyst, readily biodegradable acetic acid is not chemically oxidizable (Hermanowicz et al., 1999). The author of the study reported on in this paper has faced the same problem. The results of COD examination, obtained with the recommended and widely used open reflux titrimetric method according to PN-74 C-04578/03, were lower than expected. To support the EBPR, acetate was added to the synthetic wastewater in amounts sufficient to increase COD by about $100 \text{ mgO}_2/\text{dm}^3$. Nevertheless, the COD values determined there were only slightly higher (by about $20 \text{ mgO}_2/\text{dm}^3$) than those measured in the wastewater without acetate. The addition of the recommended catalyst did not remove these discrepancies. Finally, the "open" nature of the laboratory set for mineralization was assumed to be responsible for the inconsistencies in the results obtained.

The air or water cooler used for closing the mineralization flask did not prevent the escape of some volatile organic compounds – especially acetic acid. As a result, the "open" procedure yielded lower COD values. This was particularly noticed in raw wastewater examination.

Once the phenomenon was identified, consideration was given to the closed reflux colorimetric method, according to the EPA standard methods for wastewater examination (Eaton et al., 1995). The use of this method to eliminate the problems linked with the presence of volatile fatty acids in the probes is recommended also by other investigators (Łomotowski et al., 1999). A closed mineralization set prevented the volatilization of low-boiling compounds. The advantage of using this new method was confirmed by the analyses of standard acetate solutions.

Past experience showed that the analytical procedure could noticeably influence the quantitative determination of COD, especially when the samples contained considerable amounts of acetate. When the EBPR process is governed by specific mechanisms, the analytical procedure can influence the assessment of the kinetics of organic matter removal, as well as the concentration of phosphates, and thus disturb the PAOs' real energy budget. Relevant ideological mechanisms are depicted in Figure 1.

As shown by these plots, the real COD value in the raw wastewater and the one at the beginning of the anaerobic phase are lower when obtained with the "open" method. The same holds for the values of the ratio of total phosphorus to total COD removal efficiency ($\text{tot.rem.P}/\text{tot.rem.COD}$). This can lead to an incorrect assessment of the energy demand (organic carbon compounds) for an efficient phosphorus removal via different EBPR systems. The difference in

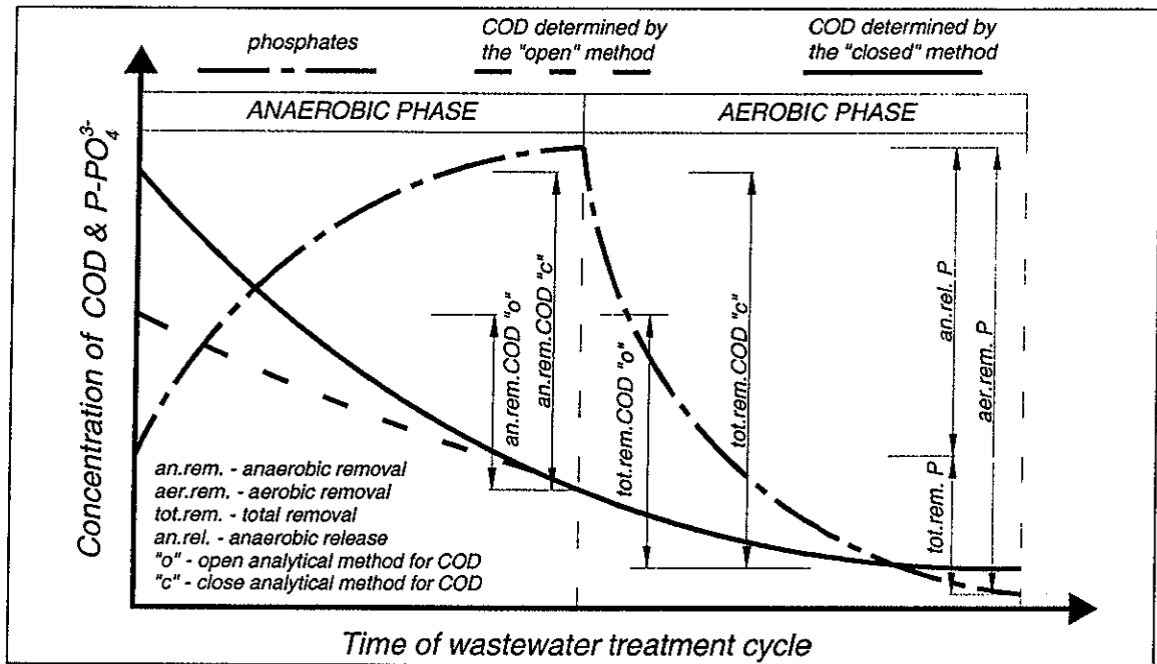


Fig. 1. Effect of the analytical procedure used for COD examination on the comparative assessment of phosphate and COD concentration variability during EBPR.

the results between the "open" and "closed" method used for COD examination may also be responsible for an incorrect assessment of the anaerobic metabolism of the PAOs. And this incorrectness will affect the conclusions about energy production from the cleavage of high-energy polyphosphate bonds, as well as those about the energy requirement for acetate transport through the cell membrane and for polyhydroxy-alkanoates storage by PAOs ($\text{an.rel.P}/\text{an.rem.COD}$).

Thus, the method used for COD examination can be one of the major factors contributing to discrepancies in the values of the comparative coefficients for COD and phosphates concentration variability in different studies of the EBPR process. But from our previous experience we know that these inconsistencies may also be due to the changeable performance parameters and conditions of the EBPR process. And that is why the elimination of the unfavorable influence of the analytical procedure for COD determination on the results obtained seems to be the key factor for a reliable assessment of the EBPR mechanisms.

An analysis of the limitations inherent in the use of "open" analytical procedures for COD determination in the study of the EBPR process has substantiated the need of using "closed" analytical sets. The results also question the usefulness of the "open" method when applied to a study where a low-boiling substance may be present in the sample, e.g. when assessing the kinetics of denitrification with methanol supply.

3.3. Procedure of calcium and magnesium examination

Standard assessment of the quality of treated wastewater does not require analyses of calcium and magnesium concentrations. As a result, there is a lack of information about the behavior of these metals during a technical-scale treatment process. However, the operation of integrated systems for C, N and P removal suggest that cations play an important role in the mechanisms of some biochemical processes.

The electrochemical balance of phase variations in the EBPR process requires that the transport of negative charges (phosphorus anions) should be accompanied by the transport of positive charges (cations). Most of the literature reports have emphasized the important role of potassium (K^+) and magnesium (Mg^{2+}) cations (Kowal et al., 1996; Mulkerrins et al., 2004; Pattarkine et al., 1999). Analyses of their concentrations have confirmed that K^+ and Mg^{2+} cations follow the same pattern of phase variability as phosphates do. In the anaerobic phase, they are released from the sludge while their concentrations in the wastewater increase. During aeration they are removed from the wastewater, and they accumulate excessively in the sludge. The observed quantitative relationship between the phase variability patterns of PO_4^{3-} , K^+ and Mg^{2+} was the starting point for the assessment of the average composition of the polyphosphates accumulated by the PAOs, according to the following stoichiometric formula: $Mg_{1/3}K_{1/3}PO_3$ (Smolders et al., 1994). The phenomenon of periodic loss of EBPR efficiency observed in real wastewater treatment plants (e.g. during episodes of rain-water flow concomitant with the dilution of magnesium and potassium) should be attributed to K^+ and Mg^{2+} limitation in the wastewater (Brdjanovic et al., 1996).

According to that part of the research, other cations like iron, sodium or calcium do not seem to considerably affect the mechanisms of the EBPR process. This idea, however, has triggered a discussion, mainly because of calcium. Some researchers have observed a co-removal of calcium and phosphorus (Carlson et al., 1997; Maurer et al., 1999; Sosnowska, 2003). Nevertheless, the role of calcium is more often identified with the mechanisms of the so-called Biologically Induced Chemical Phosphate Precipitation (BICPP) of calcium and phosphorus complexes. In principle, such process is determined by the rise in the pH of the wastewater in the aerobic phase. This rise is induced by carbon dioxide stripping that can account for the crystallization and precipitation of different phosphorus and calcium complexes.

The ascription of the phosphate crystallization phenomenon under conditions of elevated wastewater pH only to the influence of calcium does not seem to be fully convincing because magnesium is likely to exert a similar influence. Yet, examples have been reported of magnesium ammonium phosphate crystallization during the treatment of specific industrial wastewater, e.g. from pig

breeding (Suzuki et al., 2002). Such phenomena have also been observed in municipal wastewater treatment plants, but they are linked with sludge management units rather than the treatment process. Nevertheless, under favourable conditions, at elevated pH and phosphorus concentration, the BICPP mechanism can also apply to magnesium.

As one can see, the role of the cations in the EBPR process is still far from being well understood. Owing to the simultaneous presence of organic and inorganic matter, to the biological activity of activated sludge, and the interactions between different biochemical processes, it is now difficult to clearly determine the range of the BICPP process occurring in wastewater treatment systems adjusted to the technological requirements of the EBPR process.

To explain this issue, it is advisable to perform comparative analyses, which seem to be best suited for determining the kinetics of metal and phosphate concentration variation. Such research was included into our experiments, and comparative analyses produced the most interesting and probably the most valuable findings with regard to the analytical methods for EBPR process examination. The use of the simple and quick versenate titrimetric method (according to PN-91 C-04551/01 and PN-75 C-04562/01) for the assessment of calcium and magnesium concentrations in the wastewater appeared to be infeasible. The high pH of this analytical method, as well as the presence of phosphates, calcium and magnesium in the samples, favoured the precipitation of these metals and phosphates complexes.

For these reasons, in our study attempts were made to determine calcium and magnesium concentrations using methods normally recommended for wastewater and sludge analyses, i.e. flame photometry (FP) and atomic absorption spectrometry (AAS) for Ca and Mg, respectively. An example of calcium, magnesium and phosphate concentration variability obtained with these analytical methods during a treatment process cycle is given in Figure 2.

As shown by these bars, the results denied the contribution of calcium to the observed mechanisms of phosphorus removal. Calcium concentration was practically stable throughout the treatment cycle. The anaerobic release of phosphates followed by their aerobic uptake was paralleled by the same release/uptake pattern of magnesium. The calculated comparative coefficients of this variability (expressed in stoichiometric units of molMg/molP) approached 0.3, which clearly corresponded with the value incorporated in the average formula for the polyphosphates accumulated by PAOs (Smolders et al., 1994). Although the results obtained by FP and AAS did not confirm the importance of calcium to the mechanisms of phosphate removal, they substantiated the essential role of the biological mechanisms governing the EBPR and marginalized the role of chemical phosphate binding, the BICPP.

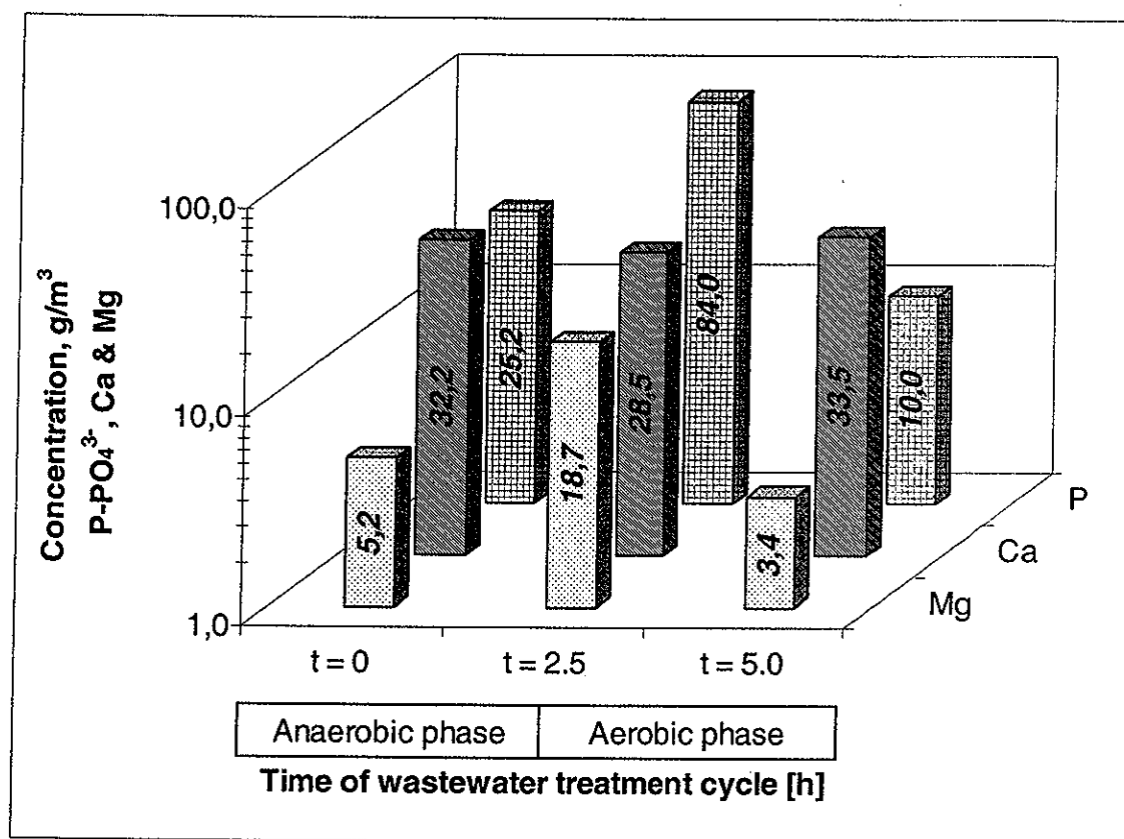


Fig. 2. Variability of calcium, magnesium and phosphate concentrations during the EBPR process cycle, determined by FP and AAS for Ca for Mg, respectively.

However, these results raised some problems with their interpretation. The value of calcium concentration in raw wastewater was substantially lower than expected. It approached 33.0 mg/dm^3 , while that in tap water (which was the basis for synthetic wastewater preparation) was close to 74.0 mg/dm^3 . The absence of visible solids in this wastewater was an indication that calcium phosphate could not have precipitated in the course of its preparation. Moreover, the variability of Ca concentration observed in wastewater analyses was not detected in parallel sludge examination. As a consequence, the convergence of the mass balance of these metals was low.

Finally, because of the problems faced when interpreting the results obtained, consideration was focused on the unfavourable influence of phosphates that were present in the sample when use was made of the FP and AAS analytical methods. The potential occurrence of this influence was also confirmed elsewhere (Eaton et al., 1995). It has been suggested that the lanthanum chloride solution should be added to compensate this negative effect. Our attempts to achieve this were a failure. The results were not reliable, which finally necessitated the search for an alternative method of Ca and Mg examination, in order to eliminate the interference of phosphates.

The possibility of using the gravimetric method as an alternative (Eaton et al., 1995; B & E Gomółkowie, 1998) was found to be promising. Though it is time-consuming, this method has been considered to be one of the most precise Ca and Mg examination procedures. The advantage of this method is the low pH of calcium oxalate precipitation, which allows the negative influence of the presence phosphates to be eliminated. Magnesium examination is performed by precipitation of magnesium ammonium phosphate at a high pH after preliminary calcium removal from the sample to be analyzed.

The bars in Figure 3 allow a comparison of variability of calcium, magnesium and phosphate concentrations in wastewater (determined by the gravimetric method).

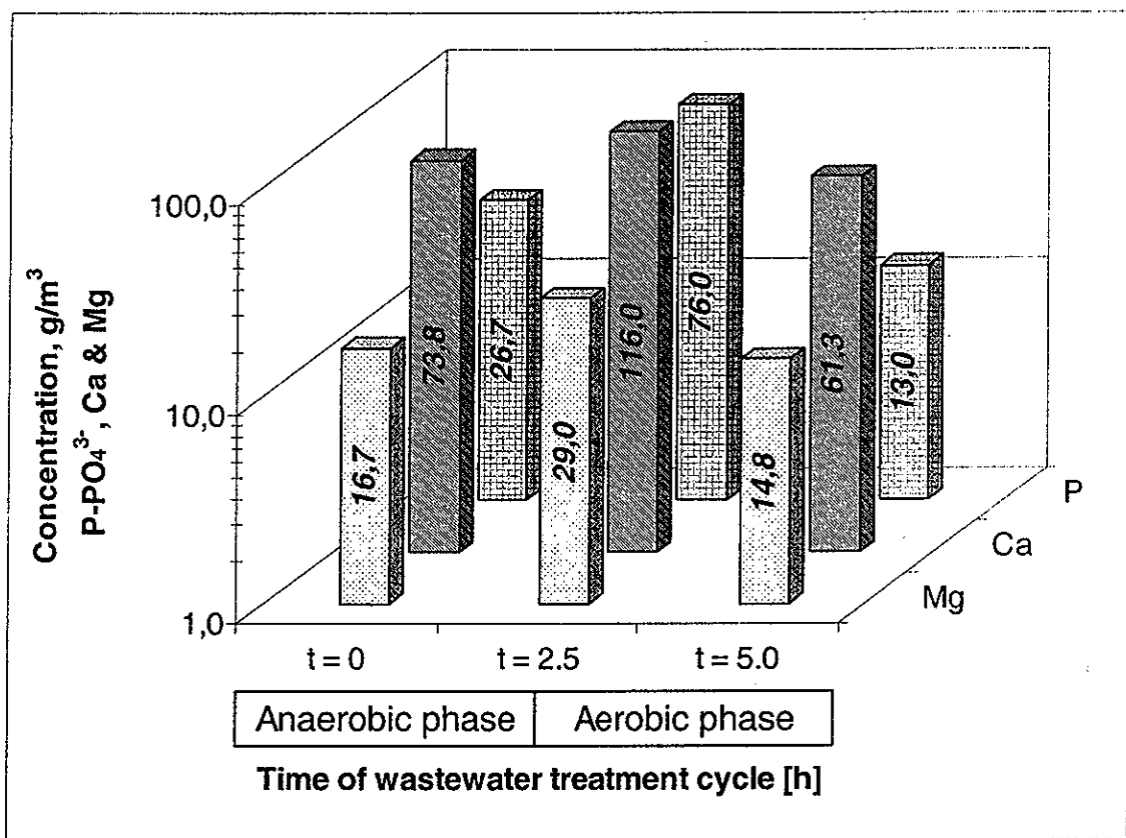


Fig. 3. Variability of calcium, magnesium and phosphate concentrations during EBPR process cycle, determined by the gravimetric method of Ca and Mg examination.

The results obtained by the gravimetric method, especially those of calcium analysis, revealed the completely different role of this metal in the observed mechanisms of phosphate removal.

Like phosphate and magnesium, calcium was found to follow an anaerobic release and aerobic uptake pattern. Such relationship was also confirmed by a similar pattern of P, Ca and Mg concentration variability detected in sludge analysis. In the anaerobic phase there was a simultaneous decrease in the concentrations of P, Ca and Mg due to their release into the wastewater. In the ae-

robic phase there was an inverse pattern. The concentrations of these elements in the sludge increased, which brought about their decrease in the wastewater. These results gave very good convergence of the mass balance in the reactors, which additionally proved the correctness of the proposed gravimetric analytical method.

As shown by the results obtained so far, the analytical method used for calcium and magnesium examination can significantly influence both quantitative and qualitative assessments of the relationship between P, Ca and Mg concentration variability in the EBPR process. As a consequence, the analytical method chosen can strongly affect the conclusions about the particular mechanisms and the real extent of phosphate removal: enhanced biological removal, i.e. the EBPR, or biologically induced chemical precipitation, i.e. the BICPP. To eliminate the unfavourable influence of phosphates when calcium and magnesium are analyzed by FP and AAS, it seems advisable to use, for example, the proposed gravimetric method as an alternative one. This might be especially useful for future analyses of the role of metal cations in phosphate removal under sequencing anaerobic-anoxic-aerobic conditions typical of modern wastewater treatment systems.

The analytical problems presented in this paper question the adequacy of the commonly recommended and widely used FP and AAS methods when they are applied to the analysis of such samples where phosphates are expected to occur in high amounts, e.g. in soils, rocks, plants or animals tissues.

4. CONCLUSIONS

Owing to the specificity of the biochemical transformations that occur in wastewater treatment systems involving EBPR, some commonly recommended and widely used analytical procedures for wastewater and sludge examination can fail to be efficient. Research on the EBPR process has revealed that the assessment of the kinetics, stoichiometry and even the essence of the phosphorus removal mechanism is influenced by a variety factors, such as the analytical procedure for COD determination, the methods used for calcium and magnesium concentration measurement, as well as the procedures for sample collection and preparation. The verification of the results and experience seems to be a key factor for the standardization of the EBPR examination methods. It probably will help better recognize the real mechanisms governing the process, the factors determining its efficiency and performance, and the interactions between other biochemical phenomena which may occur under anaerobic-anoxic-aerobic conditions in modern wastewater treatment systems.

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OCENA WYBRANYCH PROCEDUR ANALITYCZNYCH W BADANIACH
PROCESU WZMOŻONEGO BIOLOGICZNEGO USUWANIA FOSFORU
ZE ŚCIEKÓW

Streszczenie

Ze względu na złożony charakter współczesnych systemów biologicznego oczyszczania ścieków szczególnie rozpoznanie mechanizmów i wzajemnych interakcji poszczególnych procesów jednostkowych, odpowiedzialnych za przebieg oczyszczania, jest sprawą skomplikowaną. Dodatkowe przyczyny tych trudności wynikać mogą z zastosowania niektórych metod analitycznych. Głównym celem niniejszego artykułu jest zwrócenie uwagi na fakt, że w specyficznych warunkach, charakterystycznych np. dla przebiegu procesu wzmożonego biologicznego usuwania fosforu ze ścieków (ang. EBPR), powszechnie wykorzystywane i rekomendowane metody analityczne mogą okazywać się zawodne, dając niepoprawne i niewiarygodne wyniki. Dotyczy to w szczególności metod oceny wskaźnika ChZT, analizy zmienności stężeń Ca i Mg, a także procedur poboru i przygotowania prób do analiz, gdzie uzyskiwane wyniki mogą wykazywać znaczące różnice w zależności od zastosowanej metodyki. Różnice te prowadzą do nieprawidłowej oceny i wniosków na temat efektywności, stechiometrii i kinetyki procesu EBPR, zaciemniając tym samym precyzję oceny wpływu różnych czynników na proces.